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Studies on chemical bath deposited zinc sulphide thin films with special optical properties

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Abstract

Adherent and uniform zinc sulphide thin films were deposited on optical glass platelets from chemical bath containing thiourea, zinc acetate, ammonia and sodium citrate. The samples, as they were prepared were investigated by UV–vis absorption/reflection spectroscopy, fluorescence spectroscopy and X-ray diffraction. The effects of growth conditions such as reagent concentration and deposition technique (mono- and multi-layer) on optical and structural properties of the ZnS thin films have been studied. The ability of ZnS films to exhibit luminescent properties has also been investigated.

Keywords: Thin films; Chemical synthesis; Optical properties; Luminescence

1. Introduction

In recent years, there has been considerable interest in use of thin films in solar cells devices. Zinc sulphide (ZnS) is a semiconductor with a large band gap, which becomes a highly efficient luminescent material, when doped with manganese, copper or other ions [1]. ZnS thin films have also been widely studied due to their employment in many optoelectronic devices such as blue and green emitting laser diodes or electro luminescent displays.

ZnS films can be prepared by different techniques such as molecular beam epitaxy [2] sputtering [3], pulsed-laser deposition [4], metal–organic chemical vapour deposition [5], electrodeposition [6] or chemical bath deposition (CBD) [7]. Chemical bath deposition is a very attractive method for producing ZnS thin films due to its specific advantages. This method has been successfully used in the obtaining of other metal chalcogenide thin films [8–11].

The purpose of this work was to study the effects of the growth conditions, such as reagent concentration and deposition technique on optical and structural properties of the chemical bath deposited ZnS thin films. The ability of ZnS films to develop luminescent properties was also investigated.

2. Experimental part

ZnS thin films have been grown on 3 cm × 4.5 cm × 1 cm optical glass substrates by CBD technique. The following chemical bath composition was used: [zinc acetate] = 15×10^{-3} M; [sodium citrate] = 7.5×10^{-3} to 60×10^{-3} M; [ammonia] = 300×10^{-3} M; [thiourea] = 150×10^{-3} M. The glass substrates were previously ultrasonically cleaned in acetone-ethanol mixture. During the deposition, the bath temperature was maintained at 82–86 °C and the solution pH at 9.5–10.5. ZnS thin films were produced by either monolayer or multilayer technique (continuous or successive depositions). In the case of multilayer technique, after each deposition, samples were introduced into a renewed chemical bath; the total deposition time was $t = n \times m$ (number of layers × single layer deposition time). After each deposition, the powdery and less-adherent ZnS particles were removed by washing with distilled water.

In order to demonstrate the ability of ZnS films to develop luminescent properties, two different doping techniques were used to obtain light emitting materials based on ZnS/glass/ZnS heterostructures. In the first doping technique, small amounts of copper (Cu) or copper–manganese (Cu–Mn) doping ions were introduced into the chemical bath and the post-deposition annealing stage was performed at 500 °C, in nitrogen atmosphere. In the second case, Cu or Cu–Mn doping species were introduced into high-purity ZnS to form a special doping mixture for the ZnS/glass/ZnS heterostructures annealing. In this case, the thermal treatment was performed in closed system, at 550 °C.

Chemical bath deposited ZnS/glass/ZnS structures were analysed as grown or after annealing. Film thickness was determined by the micro-weighing method. An UNICAM Spectrometer UV4 was used for optical investigations

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of ZnS thin films and a Perkin-Elmer 204 Fluorescence Spectrophotometer was used to investigate photoluminescence characteristics. Crystalline structure was analysed with a standard DRON-3M Diffractometer using the filtered Kα emission of copper.

3. Results and discussion

The preparation of ZnS thin films by CBD was based on the reaction between zinc acetate, $Zn(CH_3COO)_2$ and thiourea $(NH_2)_2CS$, in alkaline medium. Sodium citrate has been employed as complexing agent as in Eq. (1):

$$Zn(CH_3COO)_2 + (NH_2)_2CS + 2OH^- \rightarrow ZnS + H_2CN_2 + 2H_2O + 2CH_3COO^- \quad (1)$$

ZnS thin films were grown by mono- and multi-layer technique. The formation of the ZnS thin films takes place either in the bulk of the solution due to the spontaneous precipitation of ZnS (homogeneous reaction), or at the surfaces of the substrates leading to the film formation (by heterogeneous reaction). The films, as they were grown show milky colour, exhibit a good uniformity and adherence and could be used as substrate to form some multilayer structures.

The influence of the complexing agent (sodium citrate) upon ZnS film thickness has been investigated at constant zinc acetate and thiourea concentration. The molar ratio of Zn^{2+} to $C_6H_5O_7{}^{3-}$ (abbreviated as Cyt^{3-}) species was varied between 1.0 and 0.5 and 1.0 and 4.0. The dependence of ZnS film thickness on sodium citrate concentration is illustrated in Fig. 1.

One can note that monolayer deposited ZnS thin films have smaller thickness than those of multilayer deposited ones for the same total deposition time. The concentration of complexing agent also influences the film quality and growth rate. Depending on Na-citrate amount, two categories of samples could be obtained: adherent and homogeneous films at high concentrations (0.03–0.06 M) and powdery and less adherent films at relatively low citrate concentration (0.005–0.015 M). The thickness of ZnS films grown onto glass substrates is dependent on deposition time (Fig. 2). Two different stages could be distinguished namely the initial linear region and the final saturation stage. This is typical for CBD growing process. For example, by doubling the deposition time, the thickness does not increase twice. This illustrates that the initial growing rate decreases with time and thickness tends to level off.

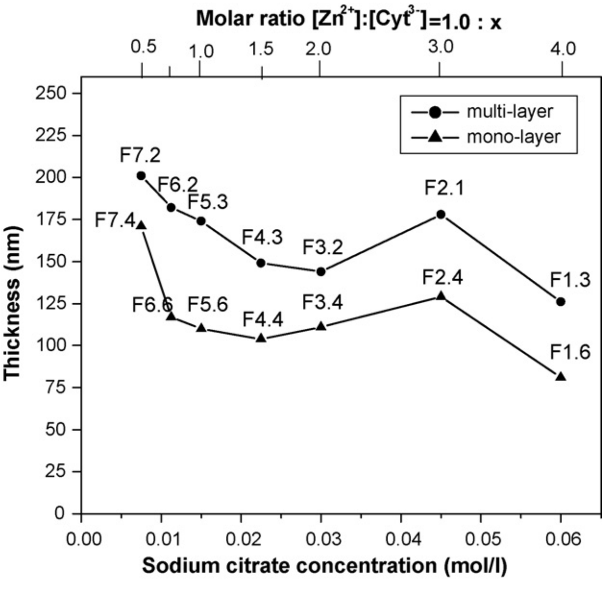

Fig. 1. Variation of ZnS films thickness with sodium citrate concentration; ($n \times m = 2 \times 1$ h for multilayer tehnique; $n \times m = 1 \times 2$ h for monolayer technique.

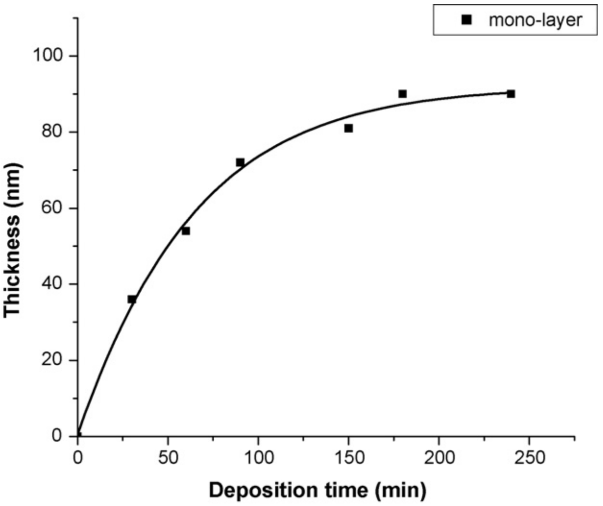

Fig. 2. Thickness as a function of deposition time for monolayer ZnS films deposited under standard conditions.

The optical transmittance of ZnS thin films is strongly influenced by the deposition technique and CBD bath composition (Fig. 3). As expected, for both deposition techniques, the ZnS/glass/ZnS structures transmittance decreases with increasing thickness. Also, the optical homogeneity of ZnS films prepared in baths with relatively low citrate concentration is poor. The thickness values and the transmittance spectra suggest that the best films quality could be obtained in bath with $[Zn^{2+}]$ to $[Cyt^{3-}]$ molar ratio of 1:3. At this reagent concentration, the films exhibit more than 70% transmittance. The optimal deposition bath, considering all ingredients, corresponds to the following reagent ratio: $[Zn^{2+}]:[Cyt^3]:[NH_3]:[\text{thiourea}] = 1:3:20:10$. These conditions were considered as standard.

The crystalline structure of ZnS thin films with ~300 nm thickness has been investigated by the X-ray diffraction (XRD) as shown in Fig. 4.

The XRD investigation of ZnS-films, as they were grown under standard conditions did not reveal any diffraction peak indicating that ZnS layer is disordered. The X-ray diffraction pattern of thermally treated ZnS/glass/ZnS structures shows a well defined (0 0 2) reflection at $2\theta = 33°$, indicating a highly textured layer with [0 0 2] direction of the ZnS phase (wurtzite-type) with crystallite dimensions of about 14 nm. The very broad diffraction at $2\theta = 26°$ is caused by nanosize crystallites and the lattice strains faults (Powder Diffractin File 5-492, JCPDS Phyladelphia, Pa., 1967).

The ability of ZnS films to develop luminescent properties was also analysed by using two different doping techniques.

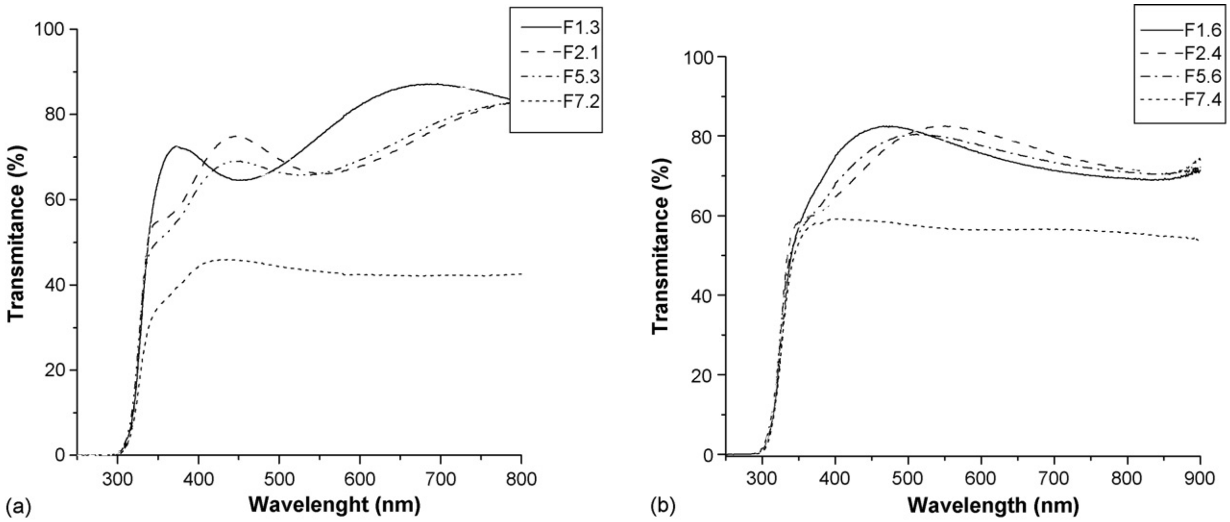

Fig. 3. Transmission spectra of ZnS/glass/ZnS structures formed by multilayer (a) and monolayer (b) technique.

Table 1
Preparation conditions of some luminescent ZnS/glass/ZnS heterostructures

Sample code	Dopant	Preparative details	Thickness (nm)[a]	Heterostructure
F9.3	Cu	Direct doping (550 °C, open system)	240	ZnS(Cu)/glass/ZnS(Cu)
F27.5	Cu	Indirect doping (550 °C, closed system)	310	ZnS(Cu)/glass/ZnS(Cu)
F10.3	Cu, Mn	Direct doping (550 °C, open system)	240	ZnS(Cu,Mn)/glass/ZnS(Cu,Mn)
F26.5	Cu, Mn	Indirect doping (550 °C, closed system)	260	ZnS(Cu,Mn)/glass/ZnS(Cu,Mn)
F28.3	–	As-grown films	300	ZnS/glass/ZnS
F28.4	–	Indirect regime (550 °C, closed system)	290	ZnS/glass/ZnS

ZnS films deposited by multilayer technique; $[Zn^{2+}]:[Cyt^{3-}] = 1:3$; $n \times m = 4 \times 1$ h.

[a] Mean value.

Some preparation details as well as the obtained heterostructures are presented in Table 1.

The light emitting properties of ZnS films are highly sensitive to the annealing regime as well as to the doping conditions. The photoluminescence (PL) spectra of Cu- and Cu, Mn-doped ZnS/glass/ZnS heterostructures prepared by direct and indirect doping are depicted in Figs. 5 and 6, respectively. The emission spectra permitted us to evaluate and compare the PL characteristics of heterostructures obtained in different annealing regime (Table 2).

The ZnS(Cu)/glass/ZnS(Cu) heterostructures exhibit more or less strong green emission related to the presence of Cu-emission centres resulting from copper incorporation into the ZnS host lattice. The emission spectrum of ZnS(Cu)/glass/ZnS(Cu) heterostructures obtained by indirect doping exhibits a strong green

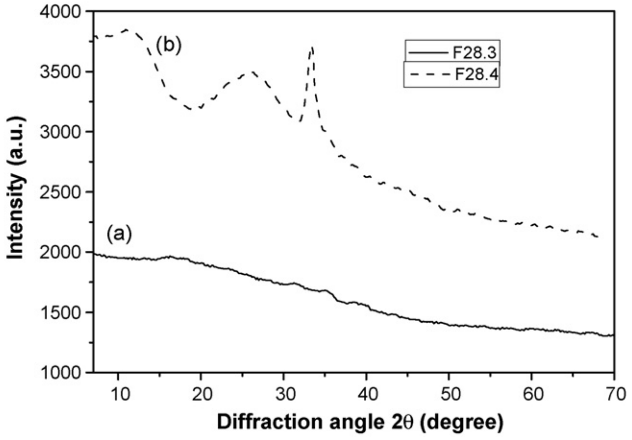

Fig. 4. XRD patterns for (a) the as grown CBD–ZnS film and (b) the annealed ZnS films (indirect doping technique).

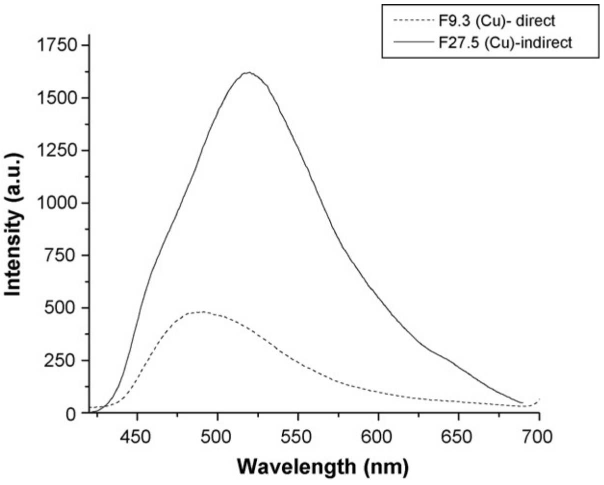

Fig. 5. Emission spectra of ZnS(Cu)/glass/ZnS(Cu) structures obtained under different annealing regime.

Table 2
Photoluminescence (PL) characteristics of some luminescent ZnS/glass/ZnS heterostructures

Sample code	Heterostructure	PL colour[a]	PL characteristics				
			Band #1		Band #2		I_{pk1}/I_{pk2}
			I_{pk1}	λ_{pk1}	I_{pk2}	λ_{pk2}	
F9.3	ZnS(Cu)/glass/ZnS(Cu)	G	480	490	420	(515)	1.1
F27.5	ZnS(Cu)/glass/ZnS(Cu)	G–Y	700	(470)	1621	520	0.4
F10.3	ZnS(Cu,Mn)/glass/ZnS(Cu,Mn)	B	2895	488	–	–	–
F26.5	ZnS(Cu,Mn)/glass/ZnS(Cu,Mn)	R	147	465	1381	578	0.1

[a] B: blue; G: green; R: red; Y: yellow; O: orange.

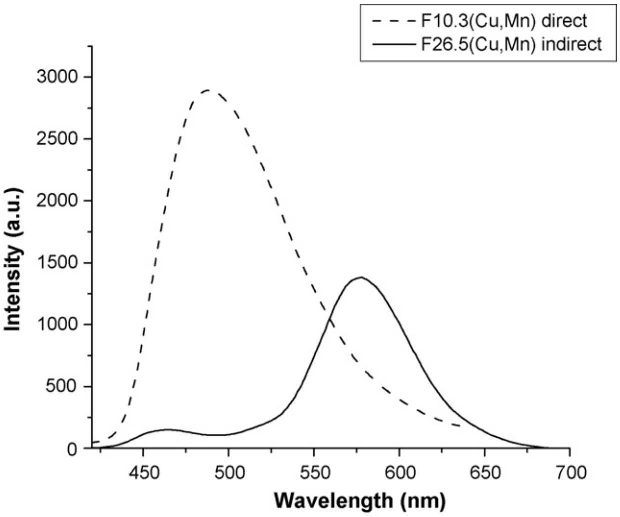

Fig. 6. Emission spectra of ZnS(Cu,Mn)/glass/ZnS(Cu,Mn) structures obtained under different annealing regime.

emission at about 520 nm; a shoulder at about 470 nm is associated with the blue self-activated emission of zinc sulphide (SA-emission centres).

The PL spectrum of ZnS(Cu)/glass/ZnS(Cu) heterostructure obtained by direct doping conditions exhibits a less intense emission band centred at about 490 nm. The position of this apparent maximum illustrate the composite nature of the spectrum that evidently contains self-activated and Cu-emission centres.

Attempts were made to Cu–Mn double activate ZnS/glass/ZnS structure by using direct or indirect doping techniques. In this case, luminescence performances are very different for samples obtained under different annealing regime. ZnS(Cu,Mn)/glass/ZnS(Cu,Mn) heterostructure obtained by direct doping regime shows strong blue emission band (∼488 nm) that could be associated with the activator presence (Cu- or Mn-emission centres). ZnS(Cu,Mn)/glass/ZnS(Cu,Mn) heterostructure obtained by indirect activating conditions, exhibits weak orange-red luminescence correlated with the presence of Mn-emission centres. The emission spectrum consists of two peaks located at ∼465 nm (associated with the presence of SA-ZnS or blue Cu-centres) and another located at ∼578 nm (associated with the presence of Mn-centres); this peak is in fact responsible for the specific orange red emission of manganese.

It is worth mentioning that the most intense luminescence is obtained by indirect doping technique. It illustrates that the additions of the doping ions into the chemical bath do not ensure a good activation of ZnS layers, contrary to the direct technique.

4. Conclusions

ZnS/glass/ZnS heterostructures with optical homogeneous chalcogenide films with thickness within 40–300 nm were prepared by CBD technique, using mono- and multi-layer deposition technique. The ability of ZnS films to develop luminescent properties was also analysed using direct and indirect doping techniques. The luminescence performances of Cu and Cu, Mn-doped heterostructures illustrate that the sample prepared in our CBD conditions shows good luminescence ability. Further investigations are needed in order to explain the observed properties and to obtain more optimum luminescent ZnS layers.

Acknowledgement

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